

Nano-structured rhodium doped SrTiO₃ – visible light activated photocatalyst for water decontamination

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Abstract:

A modified hydrothermal synthesis, avoiding high temperature calcination, is used to produce nano-particulate rhodium doped strontium titanate in a single-step, maintaining the rhodium in the photocatalytically active +3 oxidation state as shown by X-ray spectroscopy. The photoactivity of the material is demonstrated through the decomposition of aqueous methyl orange and the killing of *Escherichia coli* in aqueous suspension, both under visible light activation. A sample of SrTiO₃ containing 5 at% Rh completely decomposed a solution of methyl orange in less than 40 minutes and *E. coli* is deactivated within 6 hours under visible light irradiation.

Keywords: photocatalysis • anti-microbial • water decontamination • doped titanates

1. Introduction

Photocatalysis by semiconductor particles has been an active area of research since the 1970's.[1] The main drive for this work has been solar energy conversion via water splitting. More recently attention has focused on the use of photocatalysts for water treatment, specifically the photo-oxidation of dyes and organic contaminants.[2] There are also an increasing numbers of reports about the application of photocatalysts, especially TiO₂, for the treatment of bacteria and antimicrobial benefits.[3, 4]

TiO₂ is the most widely studied photocatalyst due to its high efficiency and stability when used as a photocatalyst in water however it has a large band gap and is restricted to UV photocatalysis.[1, 5] In applications using sunlight, this limits it to utilising less than 5% of the solar spectrum and there is significant interest in extending the response of the material to visible light by doping with transition metals.[5, 6] In solar energy conversion Kudo and others have shown that Rh-doped SrTiO₃ can be an efficient photocatalyst with visible light.[7] The role of Rh in this material is complicated by the availability of multiple oxidation states on Rh, particularly Rh³⁺ and Rh⁴⁺. SrTiO₃ containing Rh⁴⁺ tends to be less photochemically active than the material containing only Rh³⁺. [8] In this work we have modified the hydrothermal protocol of Kato *et. al.* to avoid the need for high temperature calcination.[9]. This produces a high surface area material and limits the amount of unwanted Rh⁴⁺

produced during high temperature calcination. We show that this form of Rh-doped SrTiO₃, in an aqueous suspension, is an efficient photocatalyst for dye oxidation and the destruction of bacteria with visible light, both important functionalities in the remediation of contaminated water.

2. Experimental

Further experimental details are provided in the Electronic Supplementary Information

2.1 Photocatalyst synthesis

Nanostructured SrTiO₃ particles can be synthesized hydrothermally at temperatures between 100 – 200 °C by reacting nanoparticulate TiO₂ particles with an alkaline solution (pH > 12) of Sr(OH)₂. [9-11] SrTi_{1-x}Rh_xO₃ (x = 0; 0.01; 0.025; 0.050; 0.075; 0.1) was prepared from Aeroxide® TiO₂ P25 (Sigma Aldrich, 99.5 %), Sr(OH)₂ · 8 H₂O (Sigma Aldrich, 95 %), and RhCl₃ · xH₂O (Sigma Aldrich, Rh 38-40 %), mixed in 60 mL of distilled water at room temperature, using 2 % excess of Sr(OH)₂ · 8 H₂O. The hydrothermal reaction was carried out in a 125 mL Teflon-coated reactor, placed in an oven at 180 °C for 12 h, 5 °C/min heating rate, 2 °C/min cooling rate. The synthesized oxides were washed by centrifuging twice with 1 M acetic acid and then twice with distilled water. The centrifuged product was dried at 60 °C in air. The yield of the product was 1.2 g, 44 % when 7.5 mmol of starting materials were used. After the synthetic reaction washing the slurry with organic acid (formic acid, acetic acid) removes the residual SrCO₃ (Figure 1). [10] A further calcination step was not performed on the material.

2.2 Photocatalytic dye degradation

The photocatalytic oxidation of methyl orange (MO) was performed according to a previously reported procedure [12] using visible light irradiation ($\lambda > 420$ nm). The reaction suspensions were prepared by adding the catalyst (0.1 g) to 100 mL of 0.02 g/L MO solution. The as-made suspension was purged with air during the whole reaction. The suspension was stirred in the dark overnight to ensure adsorption/desorption equilibrium of the dye has been attained on the surface of the catalyst prior to irradiation. During irradiation, 4 mL of the suspension was removed at 15 minute intervals for subsequent MO concentration analysis following filtering through a 0.2 μ m syringe filter. The absorption spectra of the aliquots were recorded in the range of 240 - 720 nm to determine the rate of MO degradation. The pH of the MO solution remained constant throughout the time reaction during the decomposition process (pH 7.2-7.7), no further adjustment was needed.

2.3 Photocatalytic killing of *E. coli*.

Bacterial overnight cultures were set up by transferring a single bacterial colony from a streak plate to 10 mL Luria-Bertani (LB) broth for *E. coli* (strain MC1061) [13] and incubated at 37 °C overnight with shaking at 200 rpm. The overnight bacterial cultures were then sub-cultured and 250 μ L was transferred to 10 mL fresh LB broth. The subculture was incubated at 37 °C until they reached mid-log growth phase (O.D.₆₀₀ = ~0.4-0.5), when the sub-cultures (5 μ L) were transferred to 5 mL of pre-autoclaved photocatalyst suspensions in aqueous phosphate buffered saline (PBS). For each time course experiment four samples were prepared: **L** (Light) – photocatalyst and *E. coli* sub-culture, exposed to visible light ($\lambda > 420$ nm); **D** (Dark) – photocatalyst and *E. coli*, covered to prevent exposure to light; **CL** (Control Light) – *E. coli* only, no photocatalyst, exposed to visible light ($\lambda > 420$ nm); **CD** (Control Dark) – *E. coli* only, no photocatalyst, covered to prevent exposure to light. During the reaction, the cells in the photocatalyst suspensions were stirred with magnetic stirrer bars. 100 μ L samples were taken at 0 min, 120 min, 240 min and 360 min and diluted in 900 μ L aq. PBS in a dilution series from 10⁰ to 10⁻⁵. In order to make up the cell dilutions in PBS and also to make the dilution series representative for plating, the harvested samples were vortexed and 20 μ L of each

dilution was spot plated in duplicate on LB agar plates and incubated overnight at 37 °C.[14] The bacterial colonies were then counted and colony forming units (CFU) mL⁻¹ were calculated.

3. Results and Discussion

3.1 Material Characterisation

A series of Rh-doped SrTiO₃ samples were prepared by a hydrothermal method without a further calcination step, with Rh substituting for Ti (SrTi_{1-x}Rh_xO₃). Nominal Rh contents where x = 0, 0.01 (1 at%), 0.025 (2.5 at%), 0.05 (5 at%), 0.075 (7.5 at%) and 0.10 (10 at%) were prepared. Herein samples are referred to as X-RhSTO, where X is the at% of Rh.

Powder X-ray diffraction (PXRD) data of hydrothermally synthesised SrTi_{1-x}Rh_xO₃ samples (Figure 2) can be indexed to a cubic unit cell with the $Pm\bar{3}m$ space group. The Scherrer equation gave primary SrTi_{1-x}Rh_xO₃ crystallite sizes of 29-35 nm, confirmed by transmission electron microscopy (TEM), (Figure 3). Anatase TiO₂ (29.3 2 θ , Co K α) was present as an impurity phase in all samples (Figure 2). A plot of lattice parameter against measured Rh content is shown in Figure 4. A linear evolution of lattice parameter was not observed in these samples and the lattice parameters are significantly larger than samples prepared by a solid-state route (Figure S1); a = 3.91624(9) Å for 0-RhSTO compared to 3.9056(1) Å for the equivalent solid-state sample. To explore the discrepancy between the lattice parameters of solid state and hydrothermally synthesised materials thermogravimetric analysis of the hydrothermally synthesised materials was performed (Figure 5) which showed a decrease in mass up to 450 °C corresponding to loss of hydroxyl groups, detected by FTIR as a broad peak around 3400 cm⁻¹ (Figure 1).[15] The hydroxyl groups are present through hydration of the material, as also identified in BaTiO₃,[16] in the hydrothermal method and are also required for charge compensation of Rh³⁺. This suggests there is an interplay between hydrating and charge compensating hydroxyl groups and Rh³⁺ all causing the lattice to expand by different amounts, and hence deviating from the ideal of Vegard's law.

Low magnification scanning electron microscopy (SEM) images of the materials show large (10-100 μ m), non-uniform particles with some apparent porosity (Figure 6a-b). At higher magnification these large particles were resolved into clusters of small particles with a size range of 50-100 nm (Figure 6c-d), concurring with the primary particle size calculated from the PXRD and TEM. The individual particles appear to be fused/sintered to form a porous structure in the larger clusters (Figure 6d). The morphology is consistent throughout the range of doping investigated (Figure 6 and Figure S2). Nitrogen absorption-desorption isotherms of representative samples were measured (Figure S3) to give a surface area of 23 m²/g, with a pore volume of 0.13 cm³/g for 0-RhSTO, and 27 m²/g, with a pore volume of 0.18 cm³/g, for 1-RhSTO. These characteristics are reduced from the P25 starting material which has a surface area of 54 m²/g and pore volume of 0.15 cm³/g.

X-ray absorption near-edge spectroscopy (XANES) and X-ray photoelectron spectroscopy (XPS) were used to determine the oxidation state of Rh in the bulk and on the surface of samples 1-RhSTO, 5-RhSTO and 10-RhSTO. The Rh X-ray absorption edges of the samples were compared to those of LaRhO₃ (Rh³⁺) and Sr₄RhO₆ (Rh⁴⁺), where the Rh ions are in similar coordination environments to the doped SrTiO₃ materials. XPS spectra were compared to Rh foil (Figure S4), Rh₂O₃ (Figure S5) and literature values. It was not possible to obtain a satisfactory XANES of 1-RhSTO due to the low amount of Rh, however the Rh 3d_{5/2} XPS showed a symmetrical peak shape with a binding energy of 308.5 eV (c.f. Rh 3d_{5/2} in Rh₂O₃ at 308.4 eV, Figure S5, Table S2) indicating only Rh³⁺ at the surface (Figure 7a) of this sample.

XANES spectra, collected in fluorescence geometry, for samples 5-RhSTO and 10-RhSTO are shown in Figure 8. The absorption edge, E₀, was calculated as the zero point of the 2nd derivative. Energy shifts due to misalignment of the monochromator were corrected by adjusting the relative absorption edge energy of the reference Rh⁰, measured simultaneously to the samples, to that of

the known absorption edge of Rh⁰ (23.2199 keV).[17] Corrected E₀ values for samples and standards are given in Table 1. The results suggest that Rh in these hydrothermally synthesised SrTi_{1-x}Rh_xO₃ is mostly in the +3 oxidation state.

Table 1. Rh X-ray absorption edges for standard materials and samples with x = 0.05, 0.10. Estimated errors.

Sample	E ₀ (keV)
LaRhO ₃ (Rh ³⁺ standard)	23.2218(1)
Sr ₄ RhO ₆ (Rh ⁴⁺ standard)	23.2227(1)
5-RhSTO	23.2218(2)
10-RhSTO	23.2217(2)

The Rh 3d_{5/2} XPS for the samples 5-RhSTO and 10-RhSTO show an asymmetric peak shape which could be deconvoluted into two peaks at 308.4 eV and 309.8 eV assigned to Rh³⁺ and Rh⁴⁺ species respectively (Figure 7a), confirming the presence of the photoactive Rh³⁺ species in the material and the presence of Rh⁴⁺ on the surface. Fitting parameters for XPS are given in Supplementary Information (Tables S3-S5). The doping limit of Rh into SrTiO₃ determined from solid-state synthesis was at ~ 6 at%, hence the presence of RhO₂ is unsurprising at high Rh amounts. All Rh measured binding energies match well with literature values[18-23] and standard materials (Tables S1 and S2). In the Ti 2p XPS spectral region (Figure 7b), there are 2 symmetrical peaks at 464.2 eV and 458.5 eV binding energies that can be attributed to Ti 2p_{1/2} and Ti 2p_{3/2} levels of Ti⁴⁺ in oxide.[24] No other Ti species were detected.

In the O 1s spectra the asymmetric peak is assigned to the O²⁻ species at 529.7 eV binding energy characteristic of oxide materials.[25] The shoulder observed at 531.5 eV can be attributed to the Ti-OH species [25] (Figure 7c). No O1s peak arising from carboxyl oxygen in acetic acid is observed at ~533 eV[25], indicating that the acetic acid used to remove unreacted SrCO₃, is completely removed after distilled water washing, agreeing with the FTIR measurement (Figure 1). XPS did not show any Cl 2p_{3/2} at 199.1 eV binding energy even for sample 10-RhSTO, indicating that unreacted RhCl₃ or chloride contamination was not present in the samples.

The XANES and XPS results show that the hydrothermal method, without a high temperature calcination step, produces nanosized Rh doped SrTiO₃ with the dopant mostly in the +3 oxidation state, with a general formula SrTi_{1-x}Rh_x(III)O_{3-x/2}(OH)_x.

Table 2. Calculated band gaps from fitting the Kubelka-Munk absorption spectra of X-RhSTO to a combined power law, exponential and Gaussian function (Standard error given in brackets)

Rh at% (X-RhSTO)	Fitted Band gap (eV)
0	3.19(1)
1	3.17(1)
2.5	3.19(3)
5	3.18(4)
7.5	3.09(5)
10	2.92(9)

The determination of optical band gaps directly from Tauc type plots for materials containing d-d transitions can be difficult due to overlap of the various contributions to the optical spectrum (Figure

9). Fitting of the Kubelka-Munk spectra, between 1.85 eV and 4 eV, to a power law function for an indirect band gap and an exponential function for the Urbach tail, plus a Gaussian function for the Rh d-d transitions[26] gave optical band gaps shown in Table 2 (see Figure S6 and S7 and Table S5 for fitting). The fundamental valence band to conduction band transition of the material is not changed significantly for $x \leq 0.05$ and only decreases with higher Rh loadings, $x > 0.05$. The reported band structure calculated by density functional theory (DFT)[8, 27] shows a Rh t_{2g} -state immediately above the valence band and the transition from this state to the conduction band can be assigned to the optical absorption at around 380 nm and giving rise to the yellow colour observed in the samples with $0.01 \leq x < 0.075$ (Figure 9a). At higher concentrations of Rh ($x \geq 0.075$) there was a second absorption band around 580 nm and a broad peak stretching into the near infrared with a maximum at 1300 nm both attributable to the surface Rh⁴⁺ d-d transitions.[7] The diffuse reflectance measurement of the $x \leq 0.05$ sample shows limited absorption at this region, indicating predominantly Rh³⁺ in the structure, in good agreement with the XANES and XPS results.

3.2 Photocatalytic dye degradation

The visible light activated photocatalytic efficiency of as-made samples were tested for azo-dye degradation. Figure 10 shows the photocatalytic activity for methyl orange (MO) degradation reaction using visible light ($\lambda > 420$ nm). MO has been widely used as a probe for the photocatalytic oxidation of dyes using UV light absorbing materials such as TiO₂. The results show that X-RhSTO is remarkably active as a visible light photocatalyst leading to the almost complete destruction of the dye in less than 1 hour.

The azo-dye degradation by X-RhSTO samples follows first order reaction kinetics. 5-RhSTO sample showed the best performance in photocatalytic activity. Within 30 minutes 86 % of MO was destroyed with a reaction rate, $k = 0.065 \text{ min}^{-1}$ (Figure 10a). This is comparable to the activity of P25 TiO₂ under UV illumination ($k = 0.10 \text{ min}^{-1}$);[12] P25 TiO₂ is not active under visible light irradiation.[2, 28] The high visible light activity of X-RhSTO can be attributed to the high surface area and the Rh³⁺ oxidation state of species up to $X = 5$. Increasing the doping level $X > 5$ introduces Rh⁴⁺ which can act as a recombination site for the photogenerated charge carriers and therefore suppress the kinetic reaction rate.[7] The parent compound showed no activity in MO degradation in a control experiment upon visible light exposure (Figure 10, Figure S8).

The activity of the X-RhSTO materials compares favourably to materials such as Cr-doped SrTiO₃-C₃N₄ composites ($k = 0.012 \text{ min}^{-1}$)[29] Pt-CaCu₃Ti₄O₁₂ ($k = 0.0045 \text{ min}^{-1}$)[12], that used similar conditions to those in this work; or Mo- and S- codoped TiO₂ ($k = 0.019 \text{ min}^{-1}$)[30] that was tested under more intense light irradiation.

3.3 Photocatalytic treatment of bacteria

5-RhSTO, showing the highest activity for MO degradation, was tested for the photocatalytic killing of the Gram negative bacteria *E. coli* in aqueous suspension. The suspension concentration was optimised to avoid any toxicity effect due to the photocatalyst. Figure 11 shows the viable *E. coli* population as colony forming units per mL (CFU mL⁻¹) in a PBS suspension with 5-RhSTO after sampling and plating them on Luria broth (LB) agar under control light (**CL** – visible light exposure, no photocatalyst), dark (**D** – no light exposure, with photocatalyst) and light (**L** – visible light exposure, with photocatalyst) conditions. At the catalyst suspension concentrations of 1.0 and 0.5 w/V%, toxicity appeared after 180 min as the *E. coli* growth was inhibited even under **D** condition compared to the **CL** experiment when the catalyst was not present (Figure 11a and 11b). At a photocatalyst suspension concentration of 0.1 w/V% the **D** experiment shows similar numbers of CFUs to the **CL** 180 min indicating the photocatalyst is below the toxic limit for *E. coli*, and any reduction in *E. coli*

CFUs is due to the photocatalytic activity of the material (Figure 11c). Inductively coupled plasma optical emission spectroscopy (ICP-OES) analysis of the supernatants was carried out in order to investigate the catalyst stability under the photocatalytic conditions. For this, the 5-RhSTO catalyst was suspended in PBS buffer, stirred for 24 h in the dark, centrifuged at 10,000 rpm for 10 min and the particles were filtered off with a $d > 0.2 \mu\text{m}$ pore size syringe filter. The various suspension concentrations are shown in Table 3.

Table 3 Strontium ICP-OES results from $\text{SrTi}_{0.95}\text{Rh}_{0.05}\text{O}_3$ suspended in PBS at four different concentrations [¥],

Photocatalyst Concentration (% w/V) *	Dissolved Sr concentration (ppm) ¥ ¥
0.05	2.5
0.1	5.0
0.5	17.6
1	24.7

* Freshly prepared catalyst suspension, no bacteria cells were added. ¥ No Rh or Ti was detected in any of the samples. ICP-OES detection limit for Rh = 0.1 ppm; Ti = 5×10^{-3} ppm. ¥¥ ICP-OES detection limit for Sr = 5×10^{-4} ppm

The measured data indicate Rh or Ti were present below the detection limits of the ICP-OES measurement in all of the supernatants, however, dissolved strontium was shown to increase with increasing amounts of catalyst in suspension from 0.05 – 1 % w/V respectively. *E. coli* appears to be resistant to strontium concentrations of up to 5 ppm. This concentration of strontium was consistent throughout all of the photocatalytic conditions used subsequently (Table 4) and comparable to the solubility of SrCO_3 at room temperature (11 ppm). The hydrothermally synthesised materials in this study show improved stability compared to solid-state synthesised $\text{SrTi}_{1-x}\text{Fe}_x\text{O}_3$ at suspension concentration of 0.1 % w/V, where 49 ppm of Sr was detected in the supernatant and showed significant toxic effects to *E. coli*. [4] Our studies show that ~17 ppm of Sr can result in toxic effects towards *E. coli* (Figure 11b). Moreover, it should also be noted that the ICP-OES detection limit for Rh is 0.1 ppm and the effective harmful concentration of Rh is reported to be three orders of magnitude greater. [31]

Table 4 ICP-OES results of 0.1% w/V $\text{SrTi}_{0.95}\text{Rh}_{0.05}\text{O}_3$ and 0.1% w/V SrTiO_3 suspended in PBS at various photocatalytic reaction conditions, the blank PBS solution and the LB broth in PBS ^{¥, ¥¥}

Nominal Rh at%	Conditions	Sr / (ppm) ¥ ¥
5	Autoclaved catalyst in PBS buffer + 24 h stirring in “Dark” + 2 nd autoclaving, centrifuging, filtering off the particles †*	5.023
5	Autoclaved catalyst. in PBS buffer + 24 h stirring in “Light” + 2 nd autoclaving, centrifuging, filtering off the particles †*	5.301
5	Autoclaved catalyst in PBS buffer + 24 h stirring in “Dark” + Cells + 2 nd autoclaving, centrifuging, filtering off the particles †**	6.545

5	Autoclaved catalyst in PBS buffer + 24 h stirring in "Light" + Cells + 2 nd autoclaving, centrifuging, filtering off the particles †**	4.749
N/A	Phosphate Buffered Saline (PBS)	0.010
N/A	LB broth + PBS (5 µL LB broth in 5 mL PBS)	0.024
0	Autoclaved catalyst in PBS buffer + 24 h stirring in "Dark" + Cells + 2 nd autoclaving, centrifuging, filtering off the particles †***	6.655
0	Autoclaved catalyst in PBS buffer + 24 h stirring in "Light" + Cells + 2 nd autoclaving, centrifuging, filtering off the particles †***	7.220
0	Catalyst in PBS buffer + 24 h stirring in "Dark" + no autoclaving, centrifuging, filtering off the particles *	6.030
0	Catalyst in distilled water + 24 h stirring in "Dark" + no autoclaving, centrifuging, filtering off the particles *	5.677

* Freshly prepared catalyst suspension with no bacteria cells were added. ** One repeat of L experiment of Figure 12

*** One repeat of L experiment of Figure 13. ¥ No Rh was detected in any of the samples. ICP-OES detection limit for Rh = 0.1 ppm. ¥¥ ICP-OES detection limit for Sr = 5×10^{-4} ppm.

† Autoclave: high pressure saturated steam at 121 °C, 15-20 min

To examine the impact of the catalyst on *E. coli* cell numbers over time, culture samples were taken every 120 minutes over a six hour period using 0.1 w/V% 5-RhSTO catalyst, under control dark (**CD** – no light exposure, no photocatalyst), control light (**CL** – light exposure, no photocatalyst), dark (**D** – no light, with photocatalyst) and light (**L** – light exposure, with photocatalyst) conditions. The experiments were repeated three times with representative data shown in Figure 12 and Table 5 (all repeats showed similar trends, Figure S10).

After 120 minutes the number of CFUs of *E. coli* in the **L** experiment exhibits a clear difference to the other conditions, showing no change in the number of CFUs from the initial number, compared to the **CL**, **CD** and **D** where significantly more CFUs are observed. After 360 minutes the number of CFUs in the **L** experiment significantly decreases to 9% of the original cell numbers. As a comparison when no catalyst was added to the PBS suspension in the **CD** experiment the number of CFUs increases by an order of magnitude.

Table 5. *E. coli* CFUs at T_0 and at T_{360} min with catalyst concentration of 0.1 w/V% $\text{SrTi}_{0.95}\text{Rh}_{0.05}\text{O}_3$ under control dark, control light, dark and light conditions; 300 W Xenon lamp ($\lambda > 420$ nm)

Conditions	T_0 $\times 10^5$ CFU mL ⁻¹	T_{360} $\times 10^5$ CFU mL ⁻¹
CD	2.51	20.8
CL	2.40	15.0
D	2.50	13.1
L	2.49	0.225

As a control experiment, undoped SrTiO_3 was also tested three times under the same conditions (Figure 13 and Table 6, Figure S10). There was no apparent change in CFUs across the **L** experiment, suggesting an inhibition of cell growth/division rather than killing the cells upon exposure to light in the presence of SrTiO_3 . This combination of inhibition and photocatalytic killing makes the 5-RhSTO material particularly effective in destroying *E. coli*.

Table 6. *E. coli* CFUs at T_0 and at T_{360} min with catalyst concentration of 0.1 w/V% SrTiO_3 under control dark, control light, dark and light conditions; 300 W Xenon lamp ($\lambda > 420$ nm)

Conditions	$T_0 \times 10^5 \text{ CFU mL}^{-1}$	$T_{360} \times 10^5 \text{ CFU mL}^{-1}$
CD	2.26	27.0
CL	2.63	17.6
D	2.23	9.75
L	1.95	2.25

In order to understand better the processes, fluorescent microscopy was used to visualise bacteria after plating and show possible cell death. The LIVE/DEAD BacLight Bacterial Viability Kit utilises mixtures of the SYTO[®]9 green-fluorescent nucleic acid stain and the red-fluorescent nucleic acid stain, propidium iodide. These stains differ both in their spectral characteristics and in their ability to penetrate into healthy bacterial cells. When both dyes are pre-mixed and added together to the cell culture, propidium iodide penetrates only into bacteria with damaged membranes, causing a reduction in the SYTO[®]9 stain fluorescence and stains the cells red. The killing of the cells by visible light activated 5-RhSTO was visualised by fluorescent microscopy, taken in the 6th hour of each experiment (**CD**, **CL**, **D**, **L**). In the control experiments (Figure 14a, b) the majority of cells are undamaged (fluorescing green). In the experiments containing photocatalyst (Figure 14c, d) only those exposed to light shows significant damaged cells (fluorescing red).

It was observed that after removal from suspension, cells appear to be attached and agglomerated onto the catalyst. If this occurs during the photocatalytic experiments it may have an effect on the number of countable CFUs by underestimating the viable cells in the plating measurements, especially in the **CD** experiment where it seems many live cells are agglomerated to the photocatalyst. It is also apparent that direct contact with the photocatalyst is not toxic to *E. coli* as live cells are seen agglomerated to the photocatalyst not exposed to light. Only the photocatalyst exposed to light showed significant numbers of dead cells, confirming it is mostly a photocatalytic killing of the bacteria. If there is an affinity for the bacteria to the solid photocatalyst this may add an additional mechanism for removing harmful organisms by a simple filtration of photo-active particles. Therefore the photocatalyst could be classed as a “bioactive-filter” similar to the well-known silver-deposited activated carbon fibres (ACF)[32] proposed for use in industrial processes such as drinking water filtration.

4. Conclusions

Contamination of water by organic molecules and bacteria is a growing ecological and societal issue, leading to a need for simple and effective methods of decontamination. Here we demonstrate a one-step hydrothermal synthesis of $\text{SrTi}_{1-x}\text{Rh}_x\text{O}_3$, ($0 < x < 0.1$) giving a high surface area material displaying efficient visible light activated photocatalytic activity towards organic dye degradation and anti-microbial properties in aqueous suspension. When $x \leq 0.05$ the Rh dopant is predominantly in the Rh(III) oxidation state in the bulk of the material resulting in a very efficient visible-light ($\lambda > 420$ nm) activated photocatalyst.

5-RhSTO is shown to completely oxidise a 0.02 g/L solution of methyl orange within 30 minutes under visible light illumination ($k = 0.065 \text{ min}^{-1}$), which is comparable to the activity of P25 TiO_2 under UV illumination of similar intensity ($k = 0.10 \text{ min}^{-1}$), and more active than doped TiO_2 materials showing visible light activity.

It is also shown that 5-RhSTO can act as an anti-microbial material to inhibit the growth of *E. coli* in aqueous suspension, effectively killing the bacteria within 6 hours of visible light exposure.

The material shows potential for the visible light activated photo-decontamination of water containing organic molecules and bacteria.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found in the online version at:

Underlying data for this article can be access at [10.17638/datacat.liverpool.ac.uk/155](https://datacat.liverpool.ac.uk/155)

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Figure Captions

Figure 1. FTIR spectra of acetic acid washed and distilled water washed 5-RhSTO showing the removal of residual $\text{Sr}(\text{CO}_3)_2$ (CO_3^{2-} stretch at 1468 cm^{-1}) by acetic acid washing.

Figure 2. PXRD pattern, using Co K_α radiation, of hydrothermally made Rh-doped SrTiO_3 samples with increasing Rh doping level ($x = 0.0; 0.01; 0.025; 0.05; 0.075; 0.1$). * anatase TiO_2 . Inset – zoomed section between 79° and 82° showing increasing d-spacing with increased Rh doping.

Figure 3 TEM images of 5-RhSTO showing nanoparticles with sizes 20-50 nm.

Figure 4. Plot of lattice parameter against measured Rh at% in hydrothermally synthesised Rh doped SrTiO_3 .

Figure 5. TGA plot of 0-RhSTO and 10-RhSTO, between room temperature and 800°C

Figure 6 SEM images of 0-RhSTO (**a, d**) and 5-RhSTO (**b, c**) samples, illustrating the agglomeration of the primary nanoparticulate materials.

Figure 7 (a) Fitted Rh 3d XPS spectrum of 1-RhSTO; 5-RhSTO and 10-RhSTO samples (Black line - original data, red line - Rh^{3+} fit and blue line - Rh^{4+} fit). (b) Fitted Ti 2p XPS spectrum of 1-RhSTO; 5-RhSTO and 10-RhSTO samples (Black line - original data, red curve - Ti^{4+} fit). (c) Fitted O 1s XPS spectrum of 1-RhSTO; 5-RhSTO and 10-RhSTO samples (Black line - experimental data, red curve - superposition of O_2^- species, blue curve - $-\text{OH}$ component).

Figure 8 Corrected XANES spectra of 5-RhSTO, 10-RhSTO and standard samples

Figure 9 (a) Colour change of X-RhSTO samples upon Rh doping level $X = 0; 1; 5; 10$ and **(b)** Kubelka-Munk function of as-made samples for $X = 0; 1; 2.5; 5; 7.5; 10$, (inset full spectra 300-1400 nm showing broad absorption in the NIR)

Figure 10 (a) MO degradation under visible light reaction of $\text{SrTi}_{1-x}\text{Rh}_x\text{O}_3$ ($x = 0; 0.01; 0.025; 0.05; 0.075; 0.1$) samples over a 1 hour time scale ; **(b)** Trend of MO conversion after 30 minutes using the as-made catalysts

Figure 11 Representative plots of viable *E. coli* population (colony forming units mL^{-1}) after 0 min and 180 min with catalyst concentrations of **(a)** 1% w/V of $\text{SrTi}_{0.95}\text{Rh}_{0.05}\text{O}_3$, **(b)** 0.5% w/V of $\text{SrTi}_{0.95}\text{Rh}_{0.05}\text{O}_3$ and **(c)** 0.1% w/V of $\text{SrTi}_{0.95}\text{Rh}_{0.05}\text{O}_3$ under control light (CL – white bars), dark (D – red bars) and light (L – black bars) conditions; 300 W Xenon lamp ($\lambda > 420\text{ nm}$); error bars denote the standard deviations of CFU mL^{-1} units for each experiment

Figure 12. Representative plot of CFU mL^{-1} time line measurement of *E. coli* population with concentration of 0.1% w/V of doped $\text{SrTi}_{0.95}\text{Rh}_{0.05}\text{O}_3$ under control dark, control light, dark and light conditions; 300 W Xenon lamp ($\lambda > 420\text{ nm}$); error bars denote the standard deviations of CFU mL^{-1} units for the individual experiment.

Figure 13. Representative plot of CFU mL^{-1} of *E. coli* over time were determined using a concentration of 0.1% w/V of undoped SrTiO_3 under control dark (CD), control light (CL), dark (D) and

light (L), conditions using a 300 W Xenon lamp ($\lambda > 420$ nm); error bars denote the standard deviations of CFU mL⁻¹ units the individual experiment.

Figure 14 *E. coli* cell population viability in the 6th hour of photocatalytic test detected by SYTO[®] 9 (green fluorescent) and Propidium Iodide (red fluorescent) nucleic acid stains. **(a)** Untreated cells in control dark and **(b)** control light experiments are viable. **(c)** Treated cells in dark experiment are viable. **(d)** Treated cells in light experiment are mostly destroyed; Catalyst 0.1% w/V SrTi_{0.95}Rh_{0.05}O₃; Light source 300W Xenon lamp ($\lambda > 420$ nm).

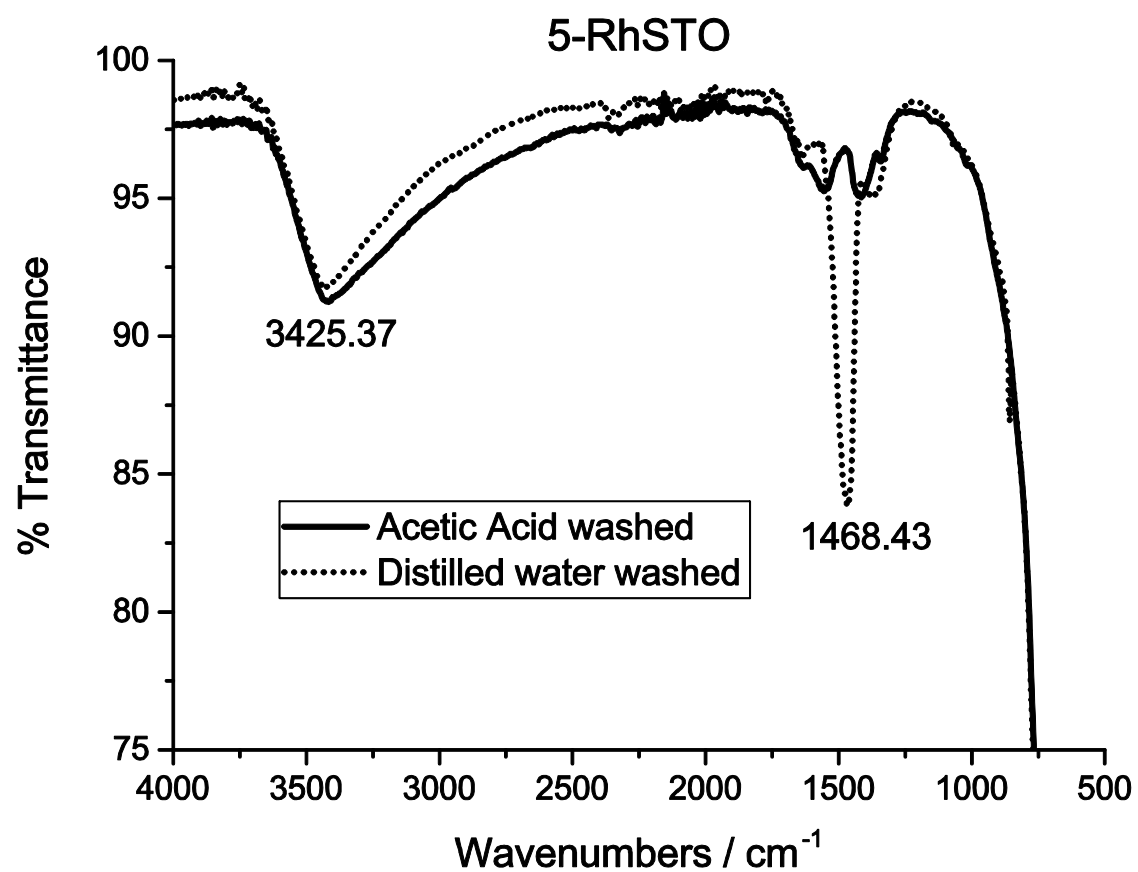


Figure 1

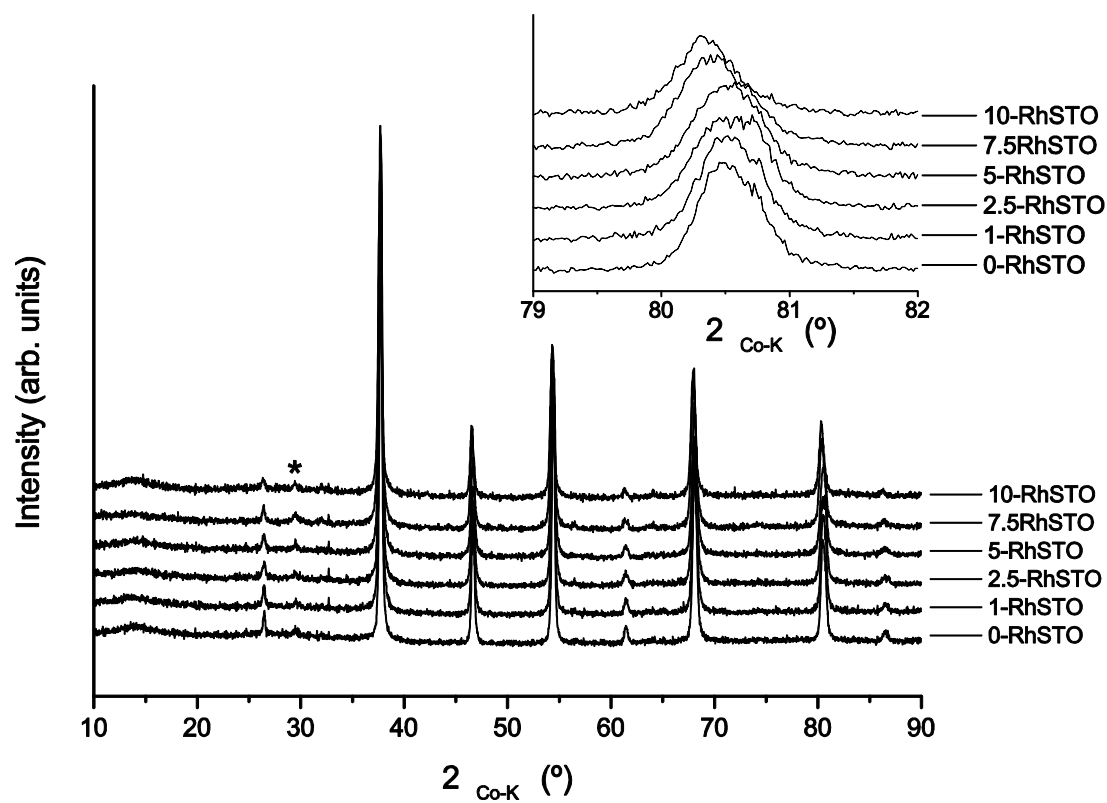


Figure 2

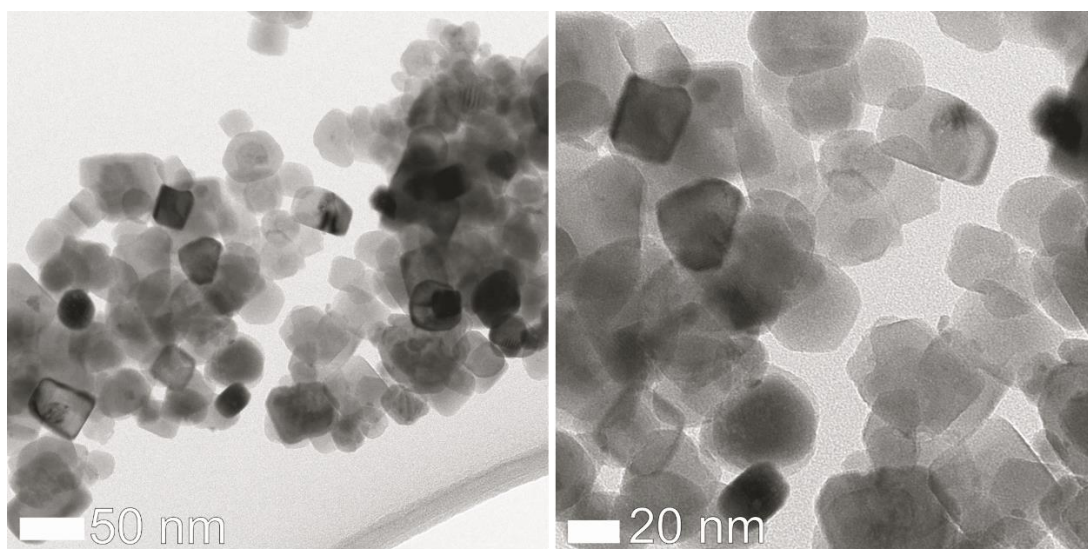


Figure 3

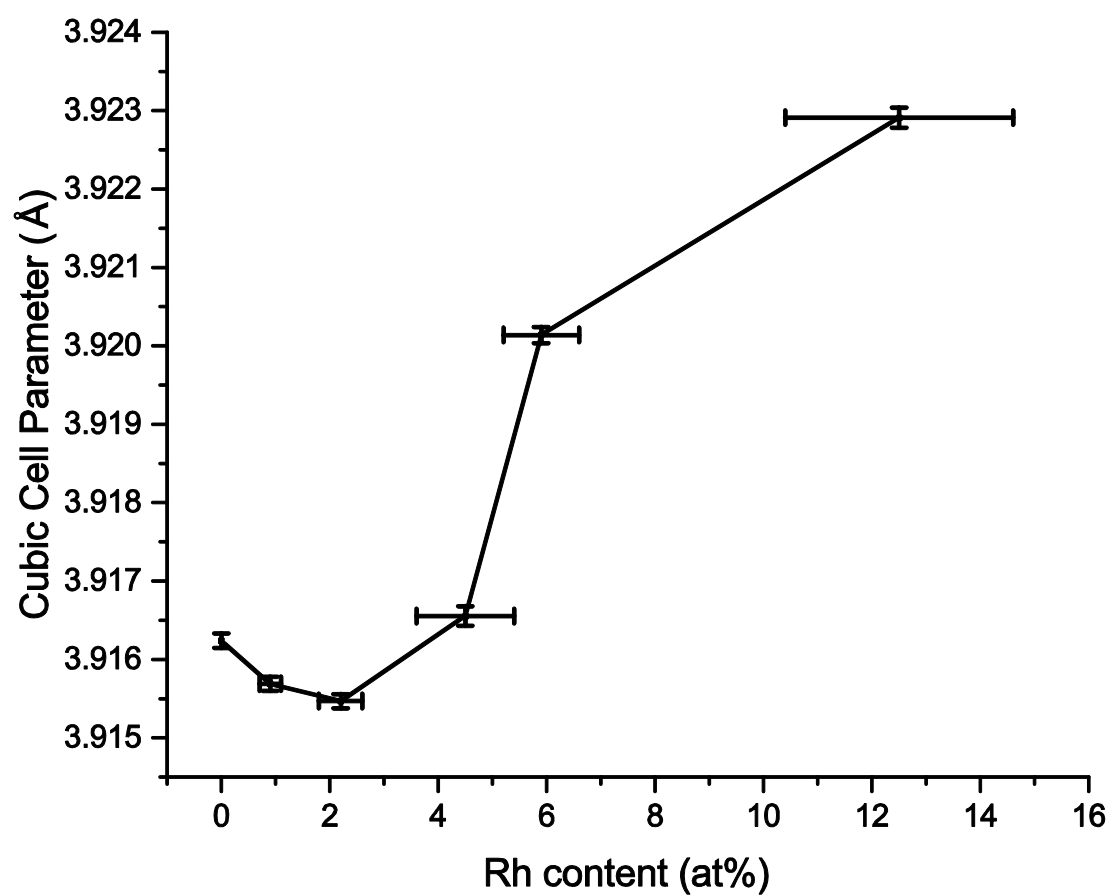


Figure 4

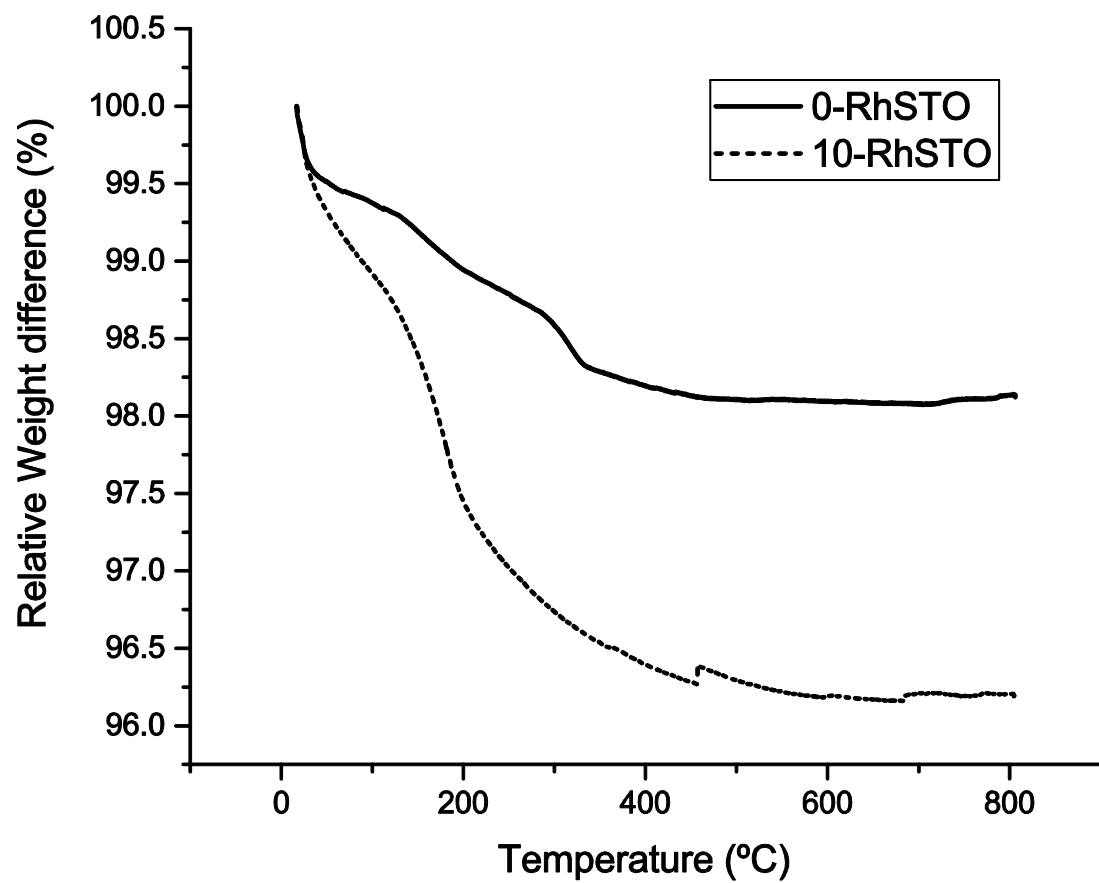


Figure 5

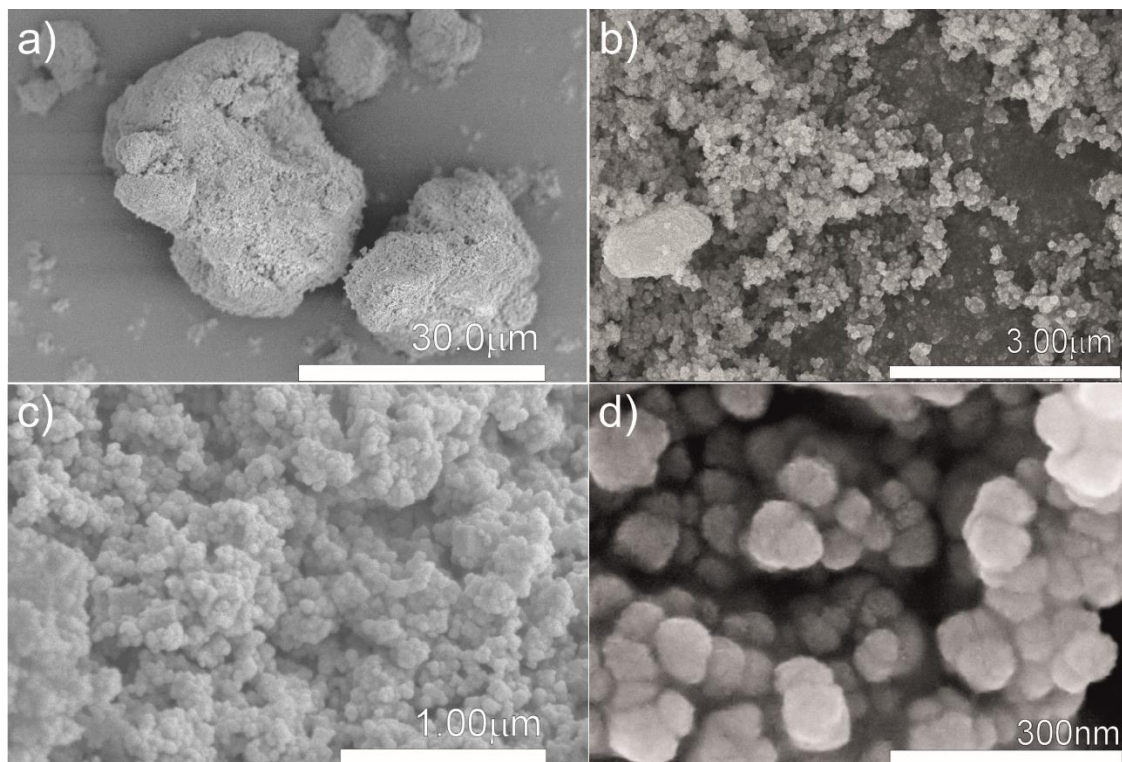


Figure 6

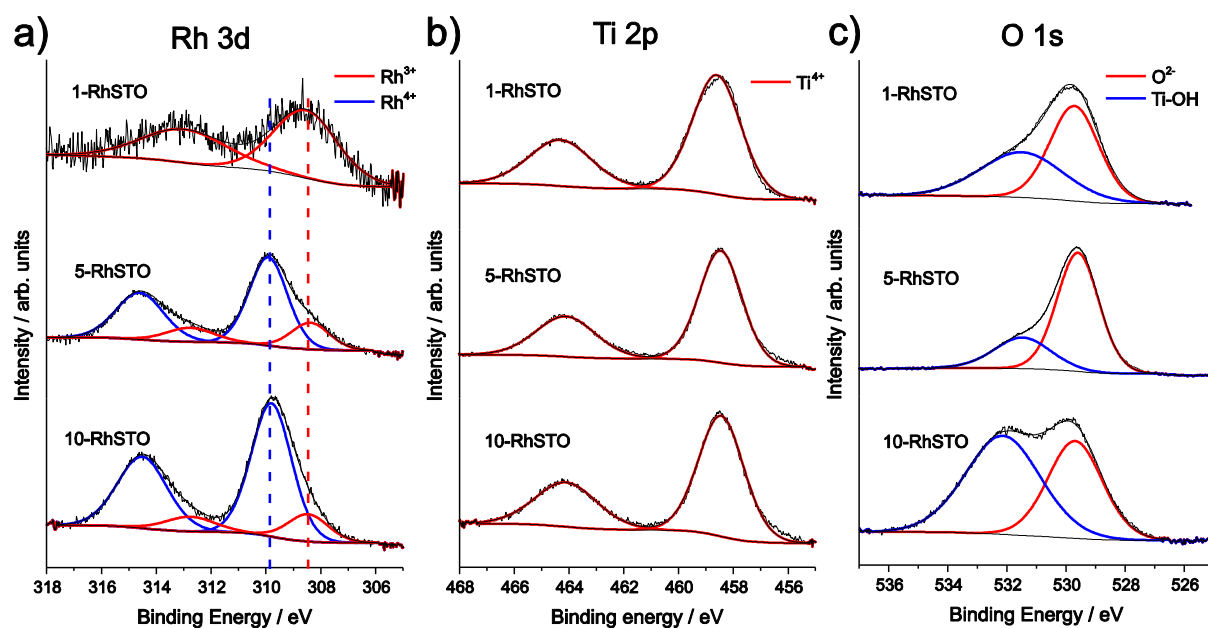


Figure 7

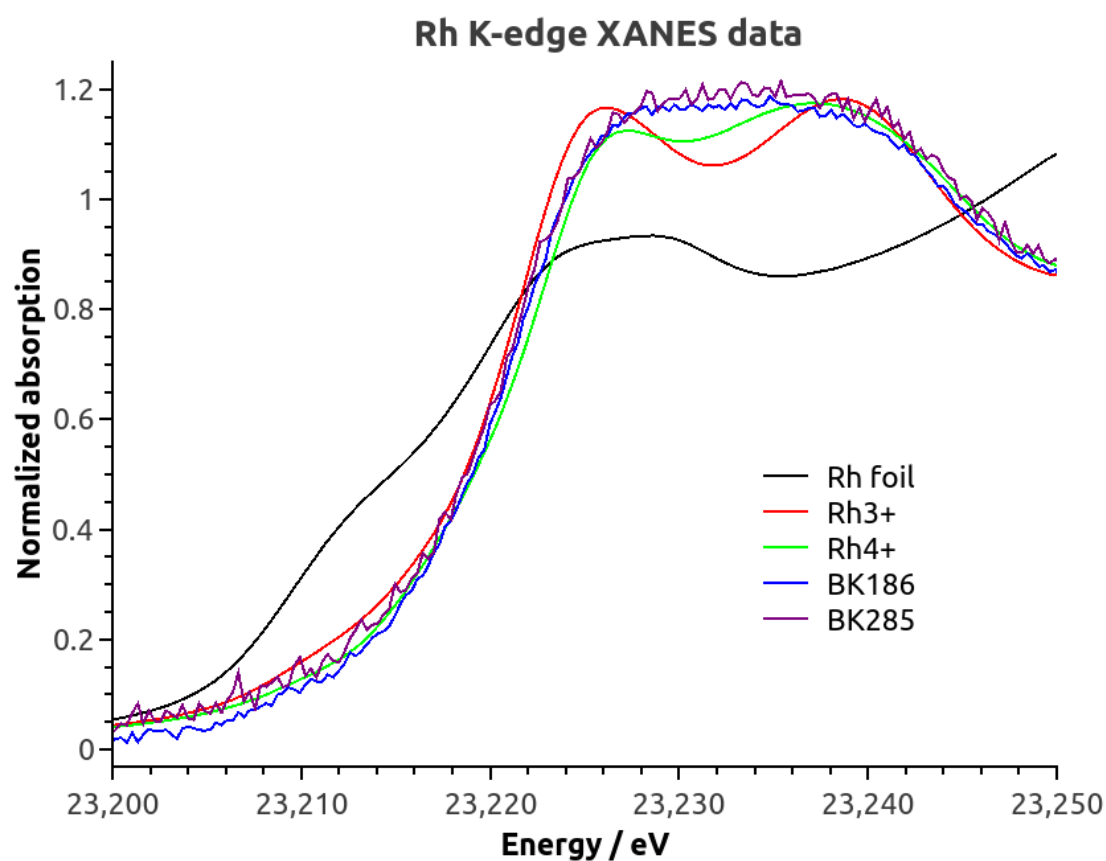


Figure 8

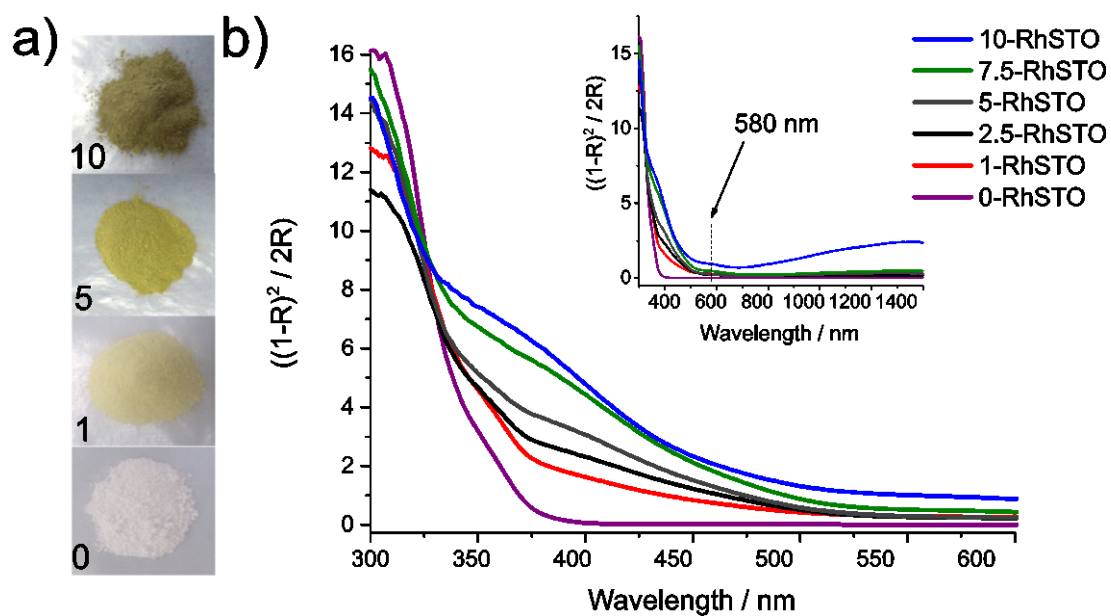


Figure 9

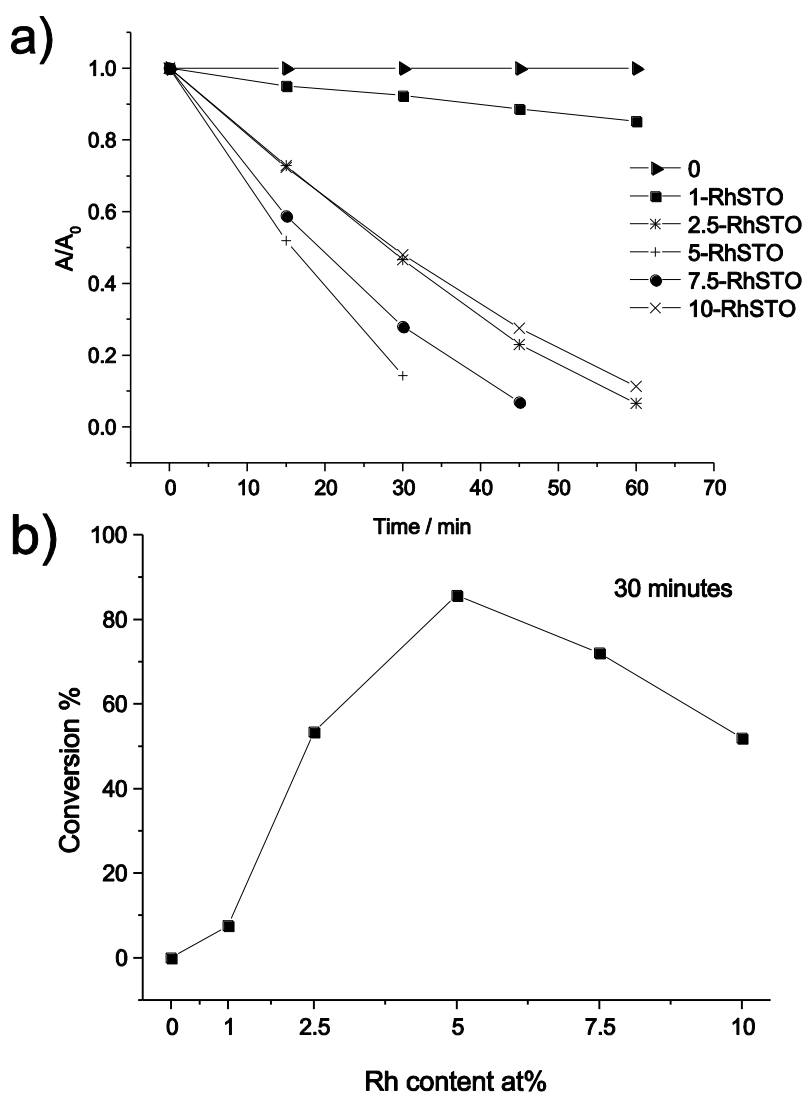


Figure 10

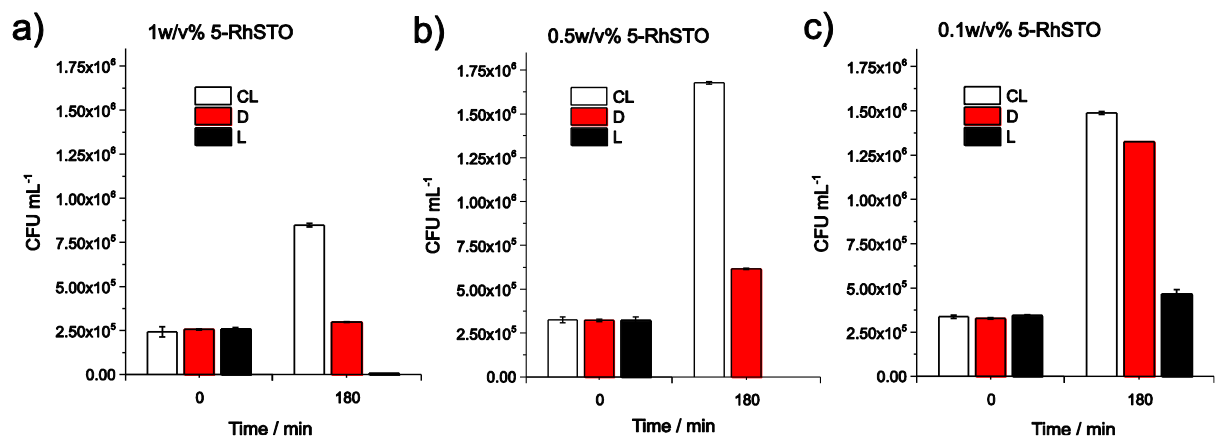


Figure 11

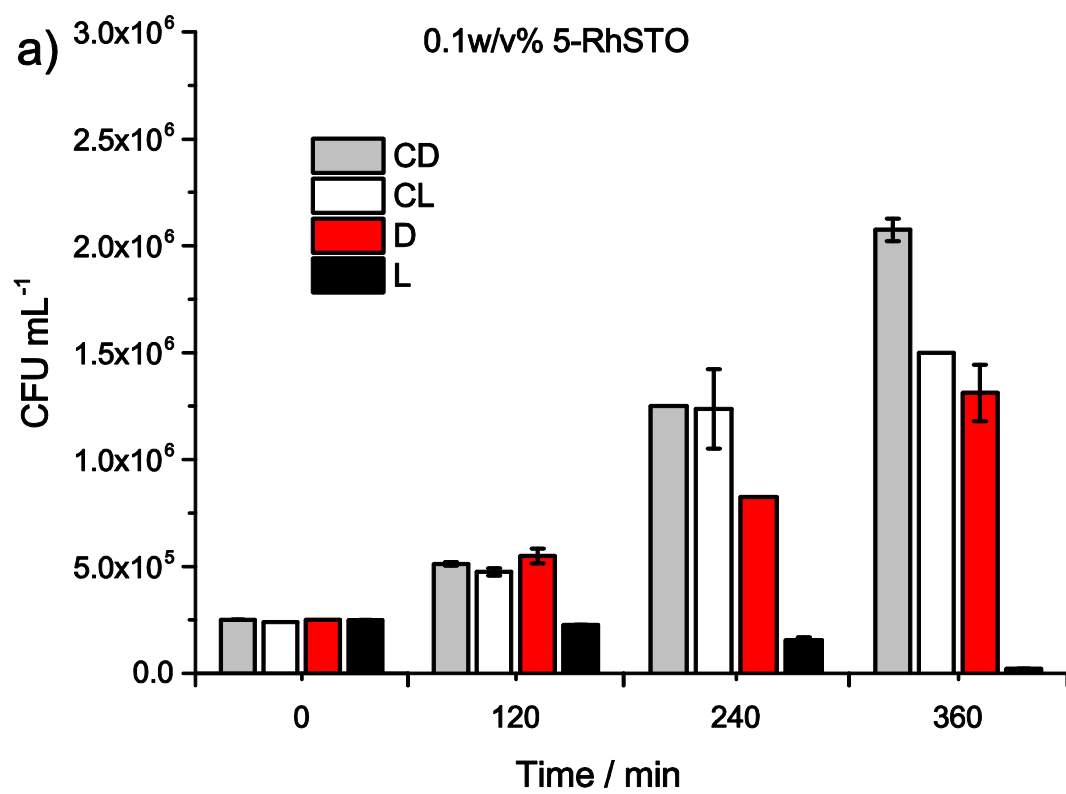


Figure 12

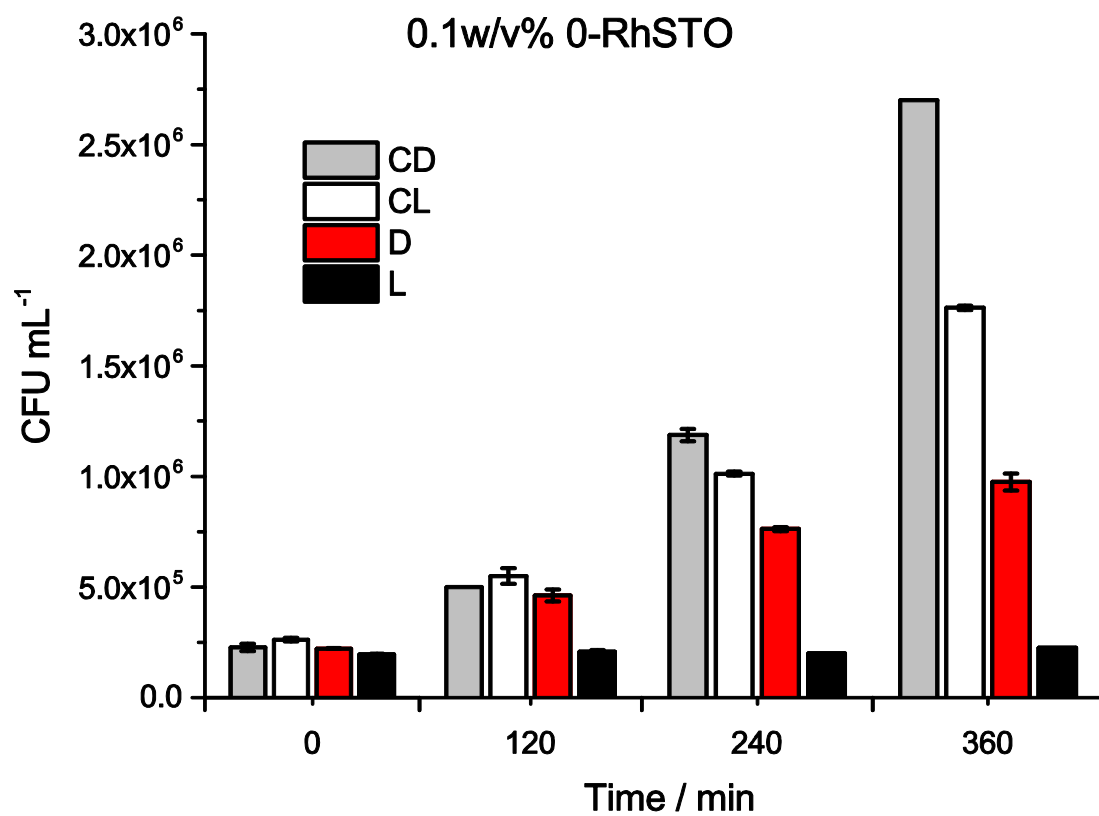


Figure 13

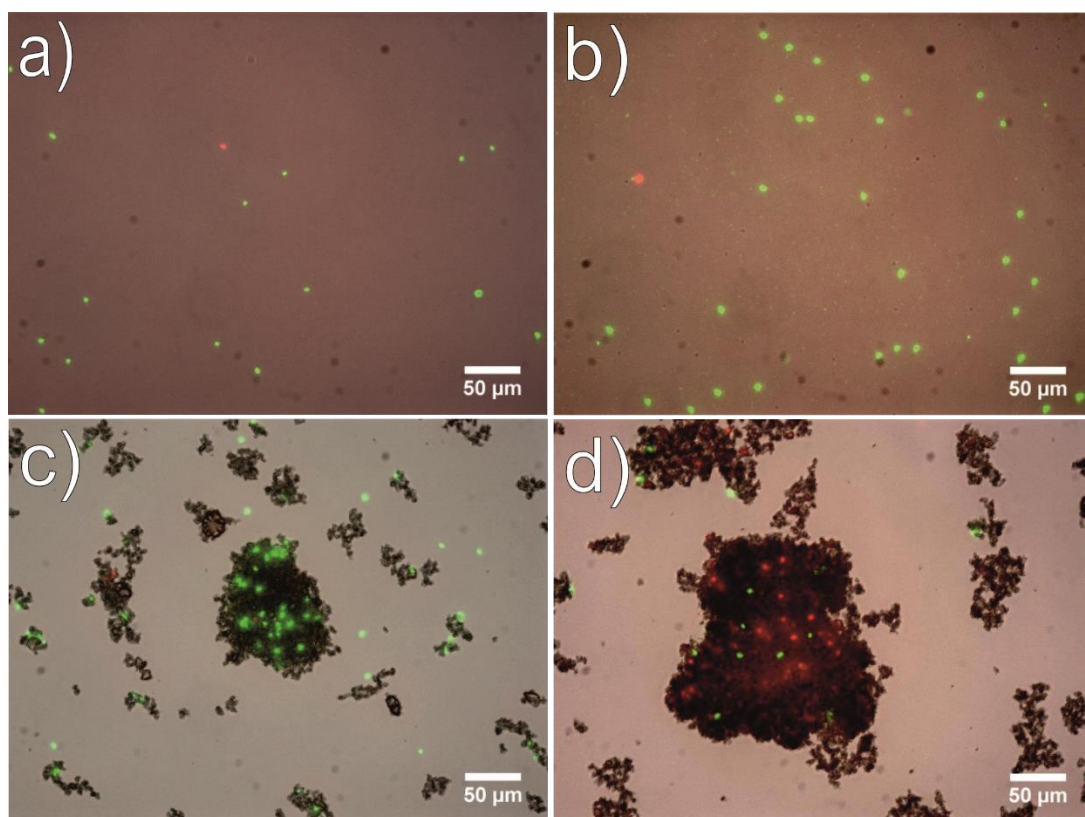


Figure 14